

Vapor-Liquid Equilibria for Ethanol and Pentane System at the Near Critical Region

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Abstract

Isothermal VLE data of n-pentane and ethanol system were obtained at near critical temperatures. A circulating type equipment with the view cell has been built and tested with the data reported by Campbell et al.[1] for the same system at 422.6K. Critical pressure was also determined from the critical opalescence of the mixtures. This mixture is very nonideal due to the association of ethanol, and the data could be correlated with sufficient accuracy by using the modified Soave-Redlich-Kwong[2] equation of state with Huron-Vidal mixing rules[3].

Keywords: experimental method; vapour-liquid equilibria; pentane; ethanol; critical state

1. Introduction

At the near critical regions, the vapor-liquid equilibrium measurements for polar and

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non-polar mixtures are necessary because the properties of such mixtures cannot be predicted from corresponding pure-component values. Therefore vapor-liquid equilibrium data for these mixtures are essential to design and operate the new process. In this work, we have measured the equilibrium pressure(P), temperature(T), liquid phase composition(x) and vapor phase composition(y) for the ethanol and n-pentane system.

2. Measurement

Materials

Ethanol is supplied by J. T. Baker with a minimum purity of 99.9 % and n-pentane was supplied by Kanto Chemical Co. Inc. with a minimum purity of 99 % (GC). In order to degas the resident air out of the chemicals, we kept the chemicals at the slightly higher pressure than the vapor pressure of each chemical.

Apparatus

This apparatus was devised to perform the vapor-liquid equilibrium experiment on the design conditions up to 400 °C and 300bar. In Figure 1, each chemical is transported into the equilibrium cell via the high pressure hand pump. The cell is installed with the quartz sight glass on both faces to observe the phase boundary, and two circulation pumps promote the equilibrium. The forced convection oven keeps the temperature of the cell and the circulation pumps uniformly. The thermometer system is the model

5614 and the model 1502 supplied by Hart Scientific Co. and the accuracy is ± 0.019 °C at 200 °C, which were calibrated for ITS-90 coefficients. The pressure transducer is the model STJE/1833-2 (range < 1000 psia) supplied by Sensotec Co., and the accuracy is $\pm 0.1\%$. The transducer was calibrated by Korea Testing Laboratory.

The chemicals are injected into the equilibrium cell after the cell is heated to the required temperature and is evacuated. Two circulation pumps mix the chemicals of both phases sufficiently because the liquid is circulated from the liquid phase to the vapor phase and the vapor is circulated reversely. When the cell reaches the equilibrium, the samples are taken on the circulation lines. The samples are transported to the GC on line, so no samples are discarded. All the sampling line out of the convection oven is electrically traced in order to prevent condensation. The detector is TCD and the column is Porapak Q.

On-line sampling technique

Figure 2 shows the sampling loop diagram. Since a high-pressure and high temperature ball valve was not commercially available, it is impossible to take on-line samples using 4 or 6 ports ball valve. So, we devised an alternative sampling procedure. On the severe condition, needle valve is more reliable than ball valve. Therefore, the arrangement of two 3-way needle valve could replace one 4-way ball valve. And, the samples with the carrier gas were heated for vaporization on the loop because the taken samples was liquid at the room temperature. The loop was evacuated after sampling in order to eliminate the resident carrier gas that caused the error in the pressure

measurement and invalidated the degassing procedure of the chemicals.

2. Thermodynamic model

For the correlation of the experimental data, we used the modified SRK model[2]:

$$p = \frac{RT}{v(v-b)} - \frac{a(T)}{v(v+b)} \quad (1)$$

where

$$a(T) = \frac{0.42747\alpha(T)R^2T_c^2}{p_c} \text{ with } \alpha(T) = 1 + (1 - T_r) \left(m + \frac{n}{T_r} \right) \quad (2)$$

and

$$b = \frac{0.08664RT_c}{p_c} \quad (3)$$

The parameter m, n was fitted to make the equation of state to calculate the experimental vapor pressure of the pure component. For ethanol, we correlated the data collection by Reid[4] at $0.7 < T_r$, and for n-pentane, the correlation by Sandarusi[2] was used. Table 1 shows the parameter values.

The Huron-Vidal[3] mixing rules for the evaluation of the parameter a, b was used. In case of SRK equation of state:

$$b = \sum_i^n b_{ii} x_i \quad (4)$$

and

$$a = b \sum_{i=1}^N x_i \left(\frac{a_{ii}}{b_{ii}} - \frac{g_\infty^E}{\ln 2} \right) \quad (5)$$

g_{∞}^E is given from the chosen excess Gibbs energy, and we used the modified NRTL model[3]:

$$g_{\infty}^E = \sum_{i=1}^n x_i \frac{RT \sum_{j=1}^n x_j G_{ji} \tau_{ji}}{\sum_{k=1}^n x_k G_{ki}} \quad \text{with } G_{ij} = b_i \exp(-\alpha_{ij} \tau_{ij}) \quad (6)$$

3. Results

The isothermal vapor-liquid measurements were determined at 500.0K, 465.4K and 422.6K for n-pentane and ethanol. The experimental data are listed in Table 2. The data at 422.6K were compared with those by Campbell et al.[1] and showed good agreement in Figure 4. With the non-randomness parameter α fixed as 0.1, the objective function for evaluating the NRTL parameter, τ_{12} , τ_{21} was the following:

$$SQ = SQP + SQY = \sum_{N=1}^{NT} \left(\frac{P_{cal} - P_{exp}}{P_{exp}} \right)^2 + \sum_{N=1}^{NT} (y_{cal} - y_{exp})^2 \quad (7)$$

The percentage of the root mean squared relative deviations between the measured and calculated pressure, $100\sqrt{SQP/NT}$, the root mean squared deviations of vapor composition of component 1, $\sqrt{SQY/NT}$, and the value of τ_{12} , τ_{21} are listed Table 3. maximum deviation of pressure does not exceed 0.64%. A comparison between the calculated and experimental values are presented in Figure 3.

Critical points were also determined from the critical opalescence of the mixture. The

coexisting compositions of pentane in the liquid and vapor phases were found to be 0.120(at 500.0K), 0.621 and 0.854(at 465.4K) mole fraction respectively. In Figure 5, PT diagram of critical locus indicates that two critical points exists at 465.4K. McCracken *et al.*[5] also reported the critical locus using the bubble-pressure and dew-pressure measurements. According to the pure component vapor pressure line of pentane and ethanol from the data bank by Reid *et al.*[4], theirs seems to indicate higher pressure and temperature. In addition, the critical locus of the mixture shows that the maximum pressure azeotrope for this system will extend to the critical point.

4. Conclusions

New arrangement of the 3-way needle valves enabled on-line GC sampling at the high temperature and pressure. The isothermal vapor-liquid equilibria for n-pentane and ethanol were obtained at near critical temperatures. The modified SRK EOS and Huron-Vidal mixing rules produced good correlation of the data.

LIST OF SYMBOLS

- a parameter in the equation of state
- b parameter in the equation of state
- g^E excess Gibbs free energy
- n number of compoments in the mixture
- NP number of data points
- P pressure

R	perfect gas constant
SQP	mean squared relative deviation of pressure,
SQY	squared and summerized deviation of vapor
T	temperature
x	mole fraction of liquid phase
y	mole fraction of vapor phase composition

Greek letters

α	non randomness parameter
τ	parameter in the mixing rule
ω	acentric factor

Subscripts

c	critical
cal	calculated
exp	experimetal

Acknowledgements

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References

- [1] Campbell, S. W., Willsak, R. A. and Thodos, J., (Vapor+liquid) equilibrium behavior of (n-pentane+ethanol) at 372.7, 397.7, and 422.6 K, J. Chem. Thermodynamics, 19, 1987, 449-460.

- [2] Sandarusi, J. A., Kidnay, A. J., and Jessavage V. F., Compilation of parameters for a polar fluid Soave-Redlich-Kwong equation of state, Ind. Eng. Chem. Process Des. Dev., 25, 1986, 957-963.

- [3] Huron, M. H. and Vidal, J., New mixing rules in a simple equation of state for representing vapor-liquid equilibria of strongly non-ideal mixtures, Fluid Phase Equilibria, 3, 1979, 255-271.

- [4] Reid, R. C., Prausnitz, J. M. and Poling, B. E., The Properties of Gases & Liquids, 4th ed., McGraw-Hill, Singapore, 1988, pp. 656-732.

- [5] McCracken, P. G., T. S. Strovick and J. M. Smith, Phase Behavior from Enthalphy Measurements Benzene-Ethylalchol and n-Pentane-Ethyl Alcohol Systems, Journal of Chemical Engineering Data, 5, 1960, 130-132.

Table 1 Critical temperature, critical pressure, and modified Soave parameters for the pure components

Substance	Tc, K	Pc (bar)	Modified Soave parameters		Reduced temp. range
			m	n	
Ethanol ^a	513.9	61.4	0.8225	0.6336	Tr > 0.7
Pentane ^b	469.6	33.7	0.7094	0.2103	0.5349 < Tr < 0.7777

a For ethanol, we correlated the parameter at Tr > 0.7 based on the data given by Reid *et al.*[4].

b Sandarusi *et al.*[2]

Table 2 Experimental VLE data for the system n-pentane(1) + ethanol(2)

T (K)	P _{exp} (bar)	P _{cal} (bar)	x _{1,exp}	y _{1,exp}	y _{1,cal}
500.0	48.55	48.51	0.000	0.000	0.000
	50.30	50.27	0.018	0.033	0.030
	53.28	53.28	0.053	0.077	0.076
	55.53	55.57	0.086	0.110	0.107
	57.05		0.114	0.122	
	57.19		0.120	0.120	
465.4	25.51	25.33	0.000	0.000	0.000
	31.00	30.74	0.079	0.172	0.177
	35.05	35.04	0.174	0.290	0.291
	38.37	38.42	0.298	0.387	0.381
	40.37	40.42	0.421	0.464	0.454
	41.34		0.535	0.543	
	41.44		0.564	0.568	
	41.45		0.613	0.615	
	41.44		0.619	0.617	
	41.44		0.621	0.621	
	37.09		0.853	0.854	
	36.27		0.885	0.868	
	34.91	34.66	0.922	0.912	0.914
	32.46	32.49	0.979	0.974	0.974

	31.53	31.59	1.000	1.000	1.000
422.6	9.748	9.674	0.000	0.000	0.000
	14.87	14.85	0.120	0.358	0.367
	12.79	12.61	0.059	0.242	0.241
	16.67	16.62	0.190	0.445	0.449
	18.21	18.35	0.311	0.520	0.525
	19.26	19.31	0.455	0.585	0.577
	19.66	19.76	0.606	0.642	0.631
	19.68	19.70	0.718	0.693	0.685
	19.30	19.16	0.817	0.754	0.753
	18.20	18.08	0.904	0.840	0.841
	15.80	15.84	1.000	1.000	1.000

Table 3 Results of VLE correlation by the modified SRK equation of state and HV mixing rule

T/K	τ_{12}	τ_{21}	$100\sqrt{SQP/NT}$	$\sqrt{SQY/NT}$
500.0	3.111	-1.921	0.06	0.002
465.4	3.179	-1.920	0.48	0.005
422.6	3.971	-2.353	0.64	0.006

Figure Caption

Figure 1. Schematic diagram of experimental apparatus. TT: thermometer, PT: pressure transducer, PG: pressure gauge

Figure 2. The sampling loop diagram.

Figure 3. Vapor-liquid equilibria for n-pentane(1)+ethanol(2) at 500.0 K, 465.4 K, 422.6K.

Figure 4. Vapor-liquid equilibria at 422.6K.(This work : ●, Campbell *et al.*[1]:)

Figure 5. Critical locus and pure vapor pressure curve for n-pentane(1) and ethanol(2).

:McCracken[5], ●: this work, — :property data bank by Reid *et al.*[4], Δ:critical points of pure components from the data bank by Reid *et al.*

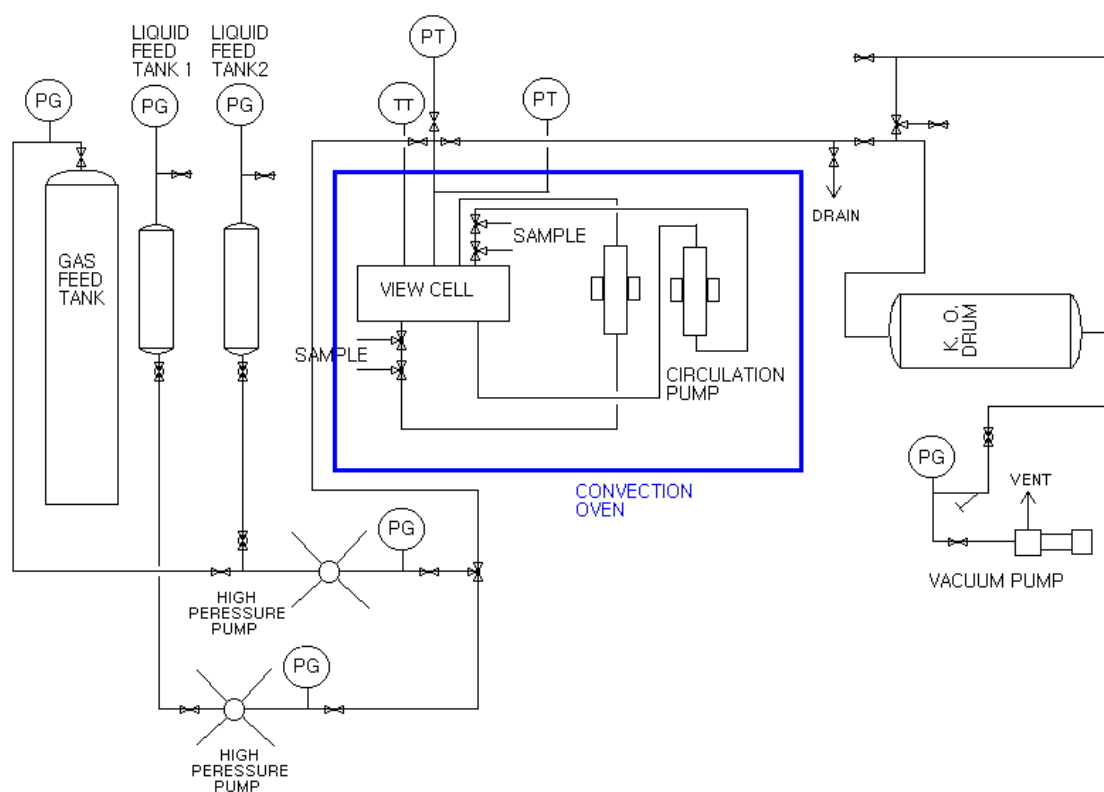


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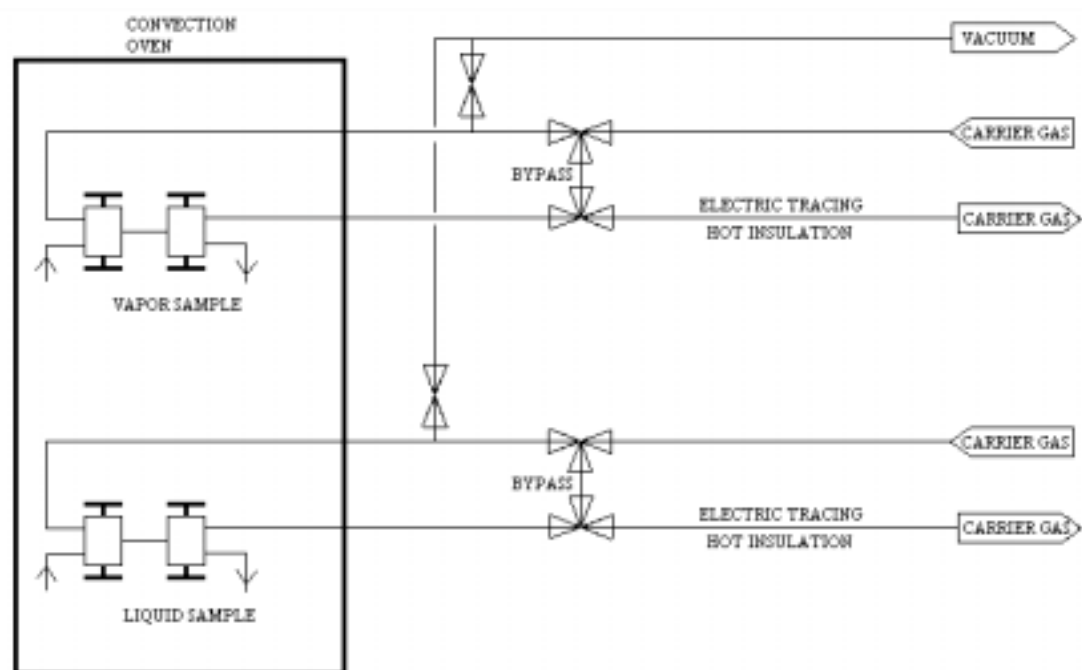


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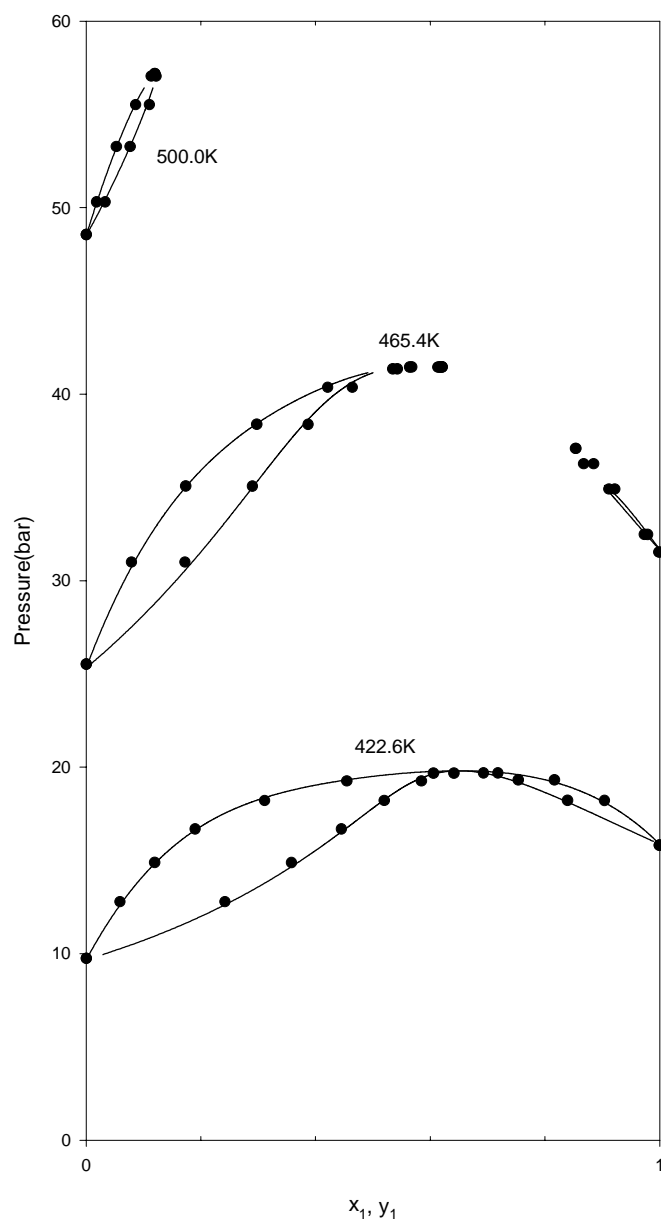


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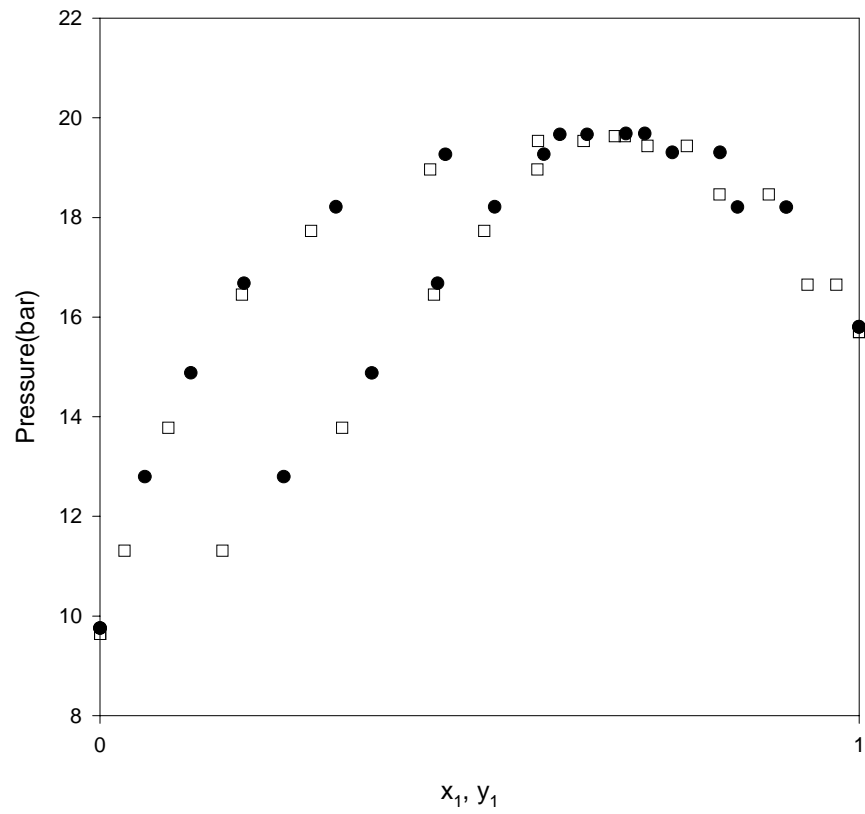


Figure 4. Vapor-liquid equilibria at 422.6K.(This work : ●, Campbell *et al.*[1]: □)

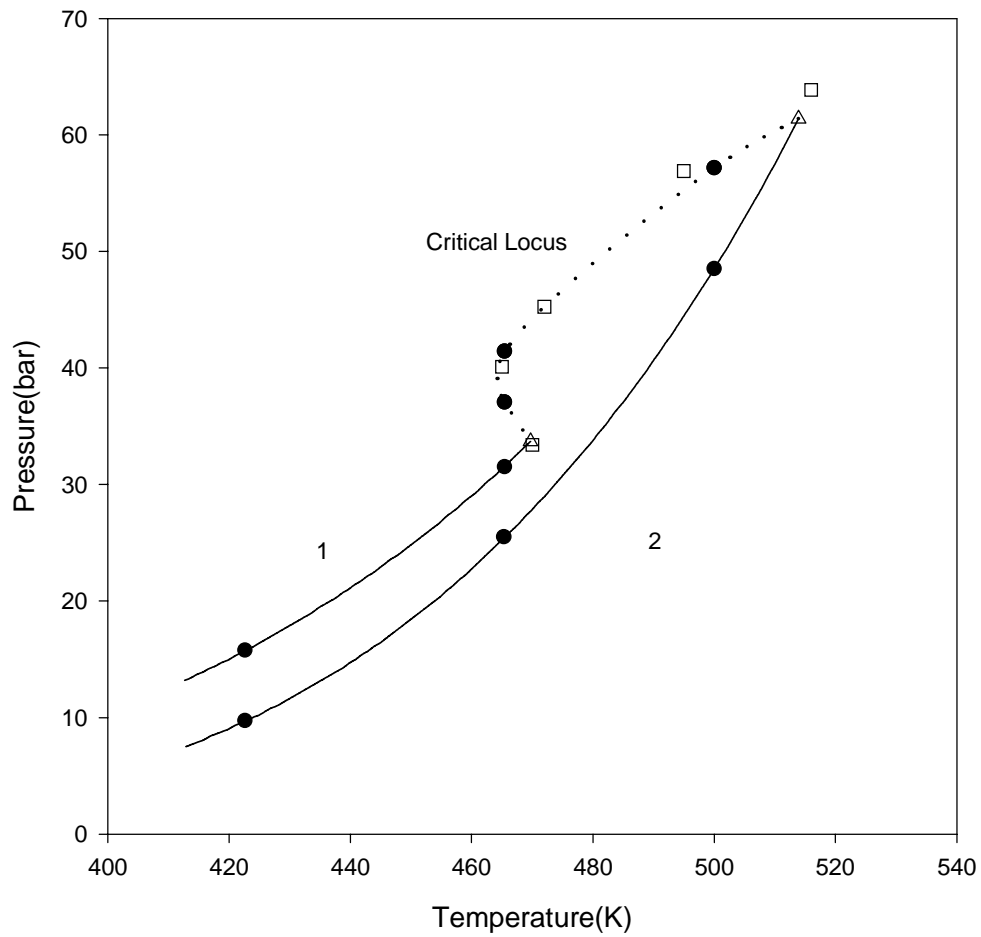


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